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X-ray Rietveld Structure Determination of Trihydroxo[dihydroxo(oxo)borato]dicopper(II), $[Cu_2\{BO(OH)_2\}(OH)_3]$

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Abstract. $M_r = 238\cdot9$, orthorhombic, *Pnma*, $a = 9\cdot4459\,(2)$, $b = 5\cdot8590\,(1)$, $c = 8\cdot6802\,(2)$ Å, $V = 480\cdot4$ Å^3, $Z = 4$, $D_m = 3\cdot1$ (pycnometric method), $D_x = 3\cdot3$ Mg m^{-3}, Cu $K\alpha_1$, $\lambda = 1\cdot54056$ Å, $\mu = 108$ cm^{-1}, $F(000) = 464$, room temperature, final $R_{wp} = 0\cdot12$, 287 reflections. The title compound belongs to the class of nesoborates and contains isolated trigonally coordinated B atoms and octahedrally coordinated Cu atoms. It appears to be the first structure for which an isolated singly charged $BO(OH)_2^-$ anion must be postulated.

Introduction. The existence of various hydrated Cu borates has been reported (Behm, 1982), but so far only two structures of hydrated Cu borates have been determined: that of the mineral bandylite by Collin (1951) and Fornaseri (1950, 1951) and that of $Na_6[Cu_2\{B_{16}O_{24}(OH)_{10}\}].12H_2O$ by Behm (1983). A summary of the literature has been given previously (Behm, 1982). The new Cu borate with formula $Cu_2\{BO(OH)_2\}(OH)_3$ was obtained in the course of a futile attempt to synthesize bandylite, $CuB(OH)_4Cl$. The presence of trigonally coordinated B and the absence of water, as revealed by infrared spectroscopy, suggested the presence of a new type of borate anion.

Experimental. *Synthesis.* $Cu_2\{BO(OH)_2\}(OH)_3$ was obtained from a solution of 42 g $NaB(OH)_4.2H_2O$ in 100 ml H_2O, to which a $CuCl_2$ solution (2·65 g $CuCl_2.2H_2O$ in 5 ml H_2O) had been added with stirring. The crystallinity of the light-blue precipitate thus obtained was improved by stirring the mixture for several days at elevated temperature. All attempts to prepare single crystals failed. The results of the chemical analysis: Cu determined by electrolysis: CuO = 65·6% (theor.: 66·6%); B as H_3BO_3 acidimetric after Cu was reduced: B_2O_3 = 16·4% (theor.: 14·6%); H as H_2O thermogravimetric: H_2O = 19·1% (theor.: 18·8%); Cl^- could not be detected.

All relevant experimental data are summarized in Table 1. The diffraction pattern was recorded on the PAD-1 diffractometer (Baerlocher & Moeck, 1975) using Cu $K\alpha_1$ radiation (Johannson-type quartz monochromator). To scale the intensities measured with different divergence slit settings, and to monitor both sample and instrument stability, the integrated intensity of the peak at 47·2° 2θ (302) was measured periodically throughout the experiment. The comparatively low background could easily be determined in the well resolved pattern and was subtracted. The pattern could be indexed on an orthorhombic cell having the dimensions reported in the *Abstract*. Careful examination of the pattern revealed that the following extinctions were present: $hk0$ $h = 2n+1$, $0k0$ $k = 2n+1$, $00l$ $l = 2n+1$. The probable space groups are *Pnma* or $Pn2_1a$. All reflections with $k = 2n+1$ are weak indicating a subcell with $b' = \frac{1}{2}b$.

Table 1. *Experimental data*

Sample container		Flat plastic holder, 1·5 × 3·0 cm
Radiation		Cu $K\alpha_1$
Pattern 2θ range (°2θ)		12–100
Step-scan increment (°2θ)		0·02
Standard peak for peak-shape function		
range 9 to 33° 2θ (hkl, 2θ)		102, 22·5
range 33 to 115° 2θ (hkl, 2θ)		332, 47·20
No. of steps (N)		4180
No. of contributing reflections		287
Absorption correction		None
Preferred orientation		None detected
Geometric restrictions		
Cu—O distance (Å)		1·97
B—O distance (Å)		1·35
O—Cu—O angle (°)		90
O—B—O angle (°)		120
No. of geometric restrictions		
starting cycles		12
final cycles		2
No. of structural parameters ($P1$)		28
No. of profile parameters ($P2$)		9
Definitions		
$R_{wp} = \{\sum_i w_i [y(\text{obs.})-y(\text{calc.})]^2/\sum_i w_i y^2(\text{obs.})\}^{1/2}$		
$R_{\exp} = [(N-P1-P2)/w_i y^2(\text{obs.})]^{1/2}$		
$R_I = \sum \lvert F(\text{obs.})-F(\text{calc.})\rvert/\sum F(\text{obs.})$		
Largest correlation matrix element	(blocked matrix)	0·42
	(unblocked matrix)	0·85
Max. Δ/σ	(blocked matrix)	1·0
	(unblocked matrix)	1·4

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The structure refinement was carried out using the X-ray Rietveld System (*XRS*82) (Baerlocher, 1982, 1984). Peaks 102 and 322 were chosen to determine the experimental peak-shape function for the lower and upper 2θ range, respectively. However, the differences between the two shapes were only minor. A plot of the 322 peak has been deposited as an illustration of the good fit between the observed peak and the calculated function. Using the latter function the numerical function of the 2θ dependence of the half width (FWHM) and the peak asymmetry were determined.

The parameters for Cu and O atoms were deduced by model building using the subcell with $b' = \frac{1}{2}b$. With the aid of the distance and angle least-squares routine in *XRS*82, starting parameters were obtained and in this way the starting phases of the weak reflections with $k = 2n+1$ determined.

The refinement in the noncentrosymmetric space group $Pn2_1a$ converged quickly to parameter values having the symmetry *Pnma*. Therefore, the refinement was continued in that space group. In *Pnma* two different choices of the origin were possible for the structure. Either the Cu atoms or the O atoms forming the square around Cu [atoms O(2) through O(5)] could be placed on the mirror plane. The two choices differ by a shift of 0·25 along the y axes. A difference Fourier map revealed that the B atom had about the same y coordinate as these O atoms. Because there are only four B atoms per unit cell, they must lie on the mirror plane. Consequently, the latter choice of origin was made, which placed the Cu atom in a general position.

The refinement converged well and all but the B—O distance restrictions could be released. If those were also released, the B moved towards the O(4) atoms resulting in unusually long bonds to O(1). The atom pairs O(2),O(3) and O(4),O(5), respectively, are related atoms in the two subcells and were strongly correlated. Except in the last cycles, they were refined in separate blocks. The protons could not be located by Fourier methods. This may in part explain why some of the O atoms have very small temperature factors. On the other hand, in X-ray Rietveld refinements the temperature factors are correlated with the background and must be interpreted with care.

The final parameters are summarized in Table 2.* The good agreement between observed and calculated data is indicated by the R values ($R_F = 0{\cdot}075$, $R_{wp} = 0{\cdot}12$ with $R_e = 0{\cdot}09$) and the plot of the observed and calculated pattern given in Fig. 1. Atomic scattering factors used were those for Cu^{2+}, O^- and B^0 from *International Tables for X-ray Crystallography* (1974).

* The figure of the standard peak function, and tables of the anisotropic temperature factors for Cu, of the IR absorption bands, of the bond-valence sum and of the observed and calculated powder data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39682 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. $Cu_2\{BO(OH)_2\}(OH)_3$ belongs to the class of nesoborates. The structure is shown in Fig. 2; interatomic distances and angles are given in Table 3. $Cu_2\{BO(OH)_2\}(OH)_3$ can be regarded as being built up of corrugated layers formed by CuO_6 octahedra and of planar BO_3 groups linking adjacent layers.

Cu has a (4+2) coordination to O atoms. Four O atoms form a square around the Cu with Cu—O bond lengths from 1·91 (3) to 1·98 (3) Å. The other two O atoms with Cu—O distances of 2·64 (1) and 2·73 (1) Å complete the positions of a strongly elongated octahedron. These octahedra build up infinite chains by sharing opposite edges of the CuO_4 squares. Neighbouring chains are connected *via* the O(1) atoms located at the apices of the octahedra, thus forming corrugated CuO_4 layers. The B atoms lie between adjacent layers and are coordinated to three O atoms with B—O distances of 1·33 (4) and 1·43 (2) Å. The O atom in the mirror plane of the BO_3 group belongs to two CuO_4 squares; the other two O atoms of the BO_3 group form the apices of the elongated CuO_6 octahedra.

The X-ray data did not permit a determination of the H atoms. The existence of the H atoms could be proved with the aid of the IR spectra, DTA measurements and interatomic distances.

Table 2. *Atomic parameters*

The temperature factors are $\times 10^2$ Å^2. Numbers in parentheses are the e.s.d.'s in units of the last significant digit given.

	Point symmetry	x	y	z	U
Cu	1	0·2494 (6)	0·002 (1)	−0·0758 (3)	2·7 (2)*
O(1)	1	0·085 (1)	0·043 (3)	0·181 (1)	0·9 (5)
O(2)	*m*	0·360 (4)	$\frac{1}{4}$	0·001 (4)	0 (1)
O(3)	*m*	0·351 (4)	$\frac{3}{4}$	0·022 (4)	0 (1)
O(4)	*m*	0·366 (3)	$\frac{1}{4}$	0·348 (5)	0·0 (1)
O(5)	*m*	0·362 (9)	$\frac{3}{4}$	0·327 (5)	0·0 (1)
B	*m*	0·006 (4)	$\frac{1}{4}$	0·166 (6)	5 (2)

* Anisotropic temperature factors for Cu have been deposited.

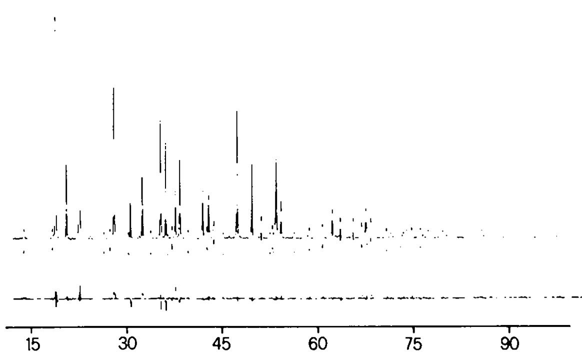

Fig. 1. Observed (upper) and calculated (middle) pattern of the Cu borate. The difference is plotted underneath with the same scale.

Table 3. *Selected distances* (Å) *and angles* (°)

Cu—O(2)	1·91 (3)	O(2)—Cu—O(3)	99 (1)
—O(3)	1·95 (3)	O(2)—Cu—O(5)	83 (1)
—O(4)	1·95 (3)	O(4)—Cu—O(3)	81 (1)
—O(5)	1·98 (3)	O(4)—Cu—O(5)	96 (1)
Average	1·95 (3)		
Cu—O(1)	2·64 (1)	O(1)—B—O(1)′	116 (3)
—O(1)′	2·73 (1)	O(1)—B—O(4)	122 (2)
B—O(1) 2×	1·43 (2)		
—O(4)	1·33 (4)		
Average	1·40 (3)		

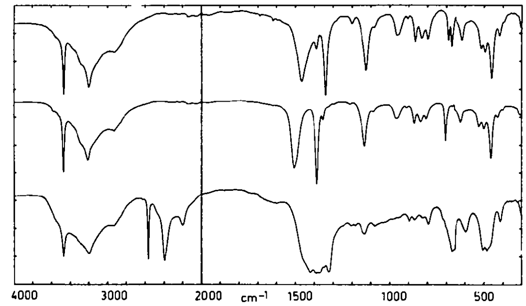

Fig. 3. Infrared absorption spectra of $4CuO.B_2O_3.5H_2O$. Top: natural isotopes, middle: 94% ^{10}B enriched, bottom: D enriched. (Powder in Rb pellets.)

From the IR spectra (Fig. 3) the presence of crystal water molecules can be excluded, since an absorption band at 1650 cm^{-1} due to the H—O—H angle bending vibration is not observed. Comparison with the spectrum of the deuterated substance shows a strong isotope effect for one B—O valence band (from 1468 to 1420 cm^{-1}) which signifies that at least one O atom must be protonated. From the O—H stretching frequencies approximate O—H—O bond lengths can be calculated using the tables given by Nakamoto, Margoshes & Rundle (1955).

DTA measurements, which show that $Cu_2\{BO(OH)_2\}(OH)_3$ is stable up to 473 K, confirm the absence of water.

Those interatomic O—O distances which do not belong to a common coordination polyhedron can be correlated to the O—H—O hydrogen-bond lengths as obtained from the O—H frequencies.

The positions of the H atoms could be inferred from Pauling's (1960) rules and the specialized borate rules given by Christ & Clark (1977). It is further assumed that the positions of the H atoms obey the *Pnma* symmetry found for the other atoms. Then four different models can be considered for the distribution of the protons among the O atoms. They have in common that the only O in a general position, O(1), must be protonated since there is no other way of assigning 20 H atoms to 20 of the 24 O atoms in a unit cell without destroying the symmetry. Three of the four O atoms in Wyckoff position *c* are bonded to two Cu atoms only with Cu—O—Cu angles between 94 (1) and 99 (1)°. The fourth is bonded to two Cu atoms and the B atom in an almost trigonal fashion with a Cu—O—Cu angle of 98 (1)° and Cu—O—B angles of 126 (1)°.

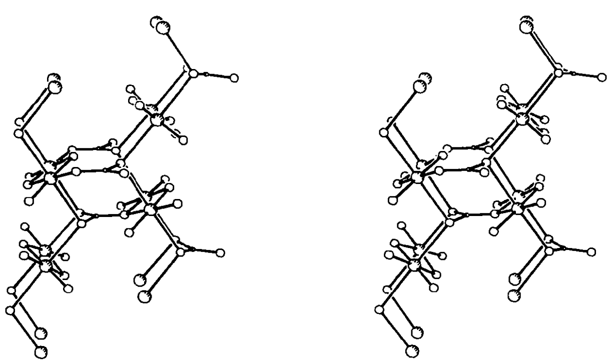

Fig. 2. Stereoscopic view of the structure (approximately parallel to *b*; *a* axis horizontal, *c* axis vertical). Shaded circles: Cu, medium-sized circles: O or OH, small circles: B.

In order to determine the unprotonated O atom the structure is approximated by a simple ionic model. Then a bond-valence sum can be calculated (table deposited). Considering Pauling's (1960) rule that electrostatic charges should be locally compensated the only O atom which can be unprotonated is O(4) whose valence sum is equalized by the two bonds to the Cu atoms and the bond to one B atom. A similar result for the H distribution would be obtained if the borate rules given by Christ & Clark (1977) were employed, but uncertainties would remain for the assignment of the two H atoms to the three O atoms of the BO_3 group, since no further coordination of the O atoms is considered. As a consequence of these considerations a new borate anion, the isolated singly charged $BO(OH)_2^-$, must be postulated.

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